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KINETICS OF OZONE DECOMPOSITION AND EXPLOSION

- USSR -

/Following is the translation of an article by S. Ya. Pshezhetskiy, S. A. Kamenetskaya, Ye. I Gribova, A. V. Pankratov, N. M. Morozov, I. N. Pospelova, A. Ya. Apin, V. N. Siryatskaya, N. A. Slavinskaya, and V. M. Cherednichenko in Problemy fizicheskoy khimii (Problems of Physical Chemistry), No 2, Moscow, 1959, pages 27-38./

(Laboratory of Gas Reaction Kinetics)

Investigation of the kinetics and mechanism of the decomposition reaction, and also the regularities of the enflaming and explosion reactions of ozone has considerable interest for the theory of chemical kinetics. The comparison of the kinetics of slow reactions with the regularities of enflaming, combustion, and explosion of ozone makes possible a test of the theory of these processes. The selection of the reaction of ozone decomposition as an object of study is accounted for by its relative simplicity which makes it possible to establish that the mechanism and kinetics of this reaction is not substantially varied under conditions of combustion and explosion, while at the same time more complicated reactions studied for this purpose show a characteristic change in the reaction mechanism in the transition from a low-temperature reaction to combustion.

### Kinetics and Mechanism of the Slow Reaction of Ozone Decomposition

The ozone decomposition reaction has stirred up especial interest in investigators in regard to the fact that, on the basis of data on the quantum yield of the photochemical reaction one can assume the existence in this process

of chain reactions. However, a small excess of the quantum yield over the value n = 2 during gaseous-phase decomposition has made this assumption somewhat doubtful.

In spite of the considerable number of studies, the kinetics and mechanism of the thermal decomposition are still not fully understood. In particular, various studies have resulted in various values for the energy of activation (from 18 to 31 kcal). It has not been clear why the pre-exponential multiplier of the second-order constant exceeds by 100 - 1000 times the number of binary collisions. Several investigators have explained this fact by the existence of chain reactions; others have related this result to the involvement of internal degrees of freedom in the activation. However, both points of view have not been sufficiently substantiated.

Earlier works devoted to the study of ozone decomposition have been examined in detail by Kassel'(1). In recent years a number of new studies have been published devoted to the study of the explosion properties(2) and the combustion(3) of ozone. A study by Benson and Axworthy has recently appeared, devoted to the investigation of the kinetics of the thermal decomposition of ozone(4). However, this study does not contain new data that is essential for the clarification of the reaction mechanism.

The first question which arises in a study of the mechanism of ozone decomposition is the question of the existence of chain reactions. Chain reactions can exist owing to the excited oxygen molecules forming in the processes:

$$O_3 + h\nu \rightarrow O_2 + O \qquad (1)$$

$$O + O_3 \rightarrow 2O_2 \qquad (2)$$
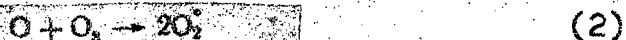
An atom chain reaction can exist on the basis of the process

$$O_2 + O_3 \rightarrow O_2 + O_2 + O \qquad (3)$$

and process (2).

We believe that chain reactions can more clearly appear in the photochemical decomposition of liquid ozone inasmuch as the associated liquid (which is the state of liquid ozone) provides more favorable conditions for the effective transmission of excitation energy through the molecules than does the gaseous state. Measurements have been carried out(5) of the quantum yield of the ozone decomposition reaction in the liquid phase at −183° C. As a result of these experiments it has been established that

the value of the quantum yield is approximately 20 molecules; at the same time according to our measurements the value of the quantum yield in the gaseous phase is about three, and according to the data of other workers, it is from two to six molecules per single quantum. Thus, in the liquid phase the photochemical decomposition of ozone evidently occurs essentially on the basis of atom chain reactions in the mechanism. However, starting with the value of the quantum yield of the gaseous-phase photodecomposition reaction of ozone it is possible to show that in the thermal decomposition of gaseous ozone chains play practically no significant role.

A characteristic feature of the ozone decomposition reaction, which up to the present has received relatively little attention is the change in the value of the kinetic constants as a measure of the subsiding of the process, that is, change in the ratio of oxygen content to ozone. This is related above all to the measured energy of activation in the reaction. Figure 1 shows the activation energy as a function of the ozone content in the mixture. The graph displays a plot using our data(6) and data obtained by other investigators(7-11). From the data presented it is clear that the effective activation energy varies as a function of the composition of the mixture, from 18 to 30 kcal. In the interval of ozone concentrations from 15 to 70 % the energy of activation is practically constant and is 24-24.5 kcal.

The pre-exponential multiplier of the second-order reaction rate constant also is a function of the mixture composition. The corresponding data is displayed in figure 2. The number of binary collisions under conditions of the experiments is of the order of 10^{11}. In concentrated ozone mixtures, therefore, the pre-exponential multiplier is less than the number of binary collisions by 10-100 times, and in diluted mixtures it is larger than the number of binary collisions by 100-10000 times. In the interval of ozone concentrations 15 to 70 % the pre-exponential multiplier is practically constant and is larger than the number of binary collisions by approximately 100 times (1.5 x x 10^{13} 1/(mole)(sec). Similar results have been obtained also in other studies.

The dependence of the energy of activation and the pre-exponential multiplier on the mixture composition (or, which is the same, the extent of change) is evidently related to the fact that the specific weight of various elementary reactions which have different energies of activation and a different pre-exponential multiplier varies as the ratio between the ozone and the oxygen contents changes. We will look at the most probable elementary stages of ozone

decomposition, and at values for the energies of activation (E) and for the pre-exponential multipliers (k_0) that we obtained for several individual stages:

		(A) k_0, л/моль·сек	E, ккал
1.	$O_3 + O_3 \rightarrow 3O_2$	$4{,}5 \cdot 10^9$	$18 \div 19$
2.	$O_3 + M \rightarrow O_2 + O + M$	—	$25 \div 26$
3.	$O + O_3 \rightarrow 2O_2$	$2{,}3 \cdot 10^9$	$5{,}0$
4.	$O + O_2 + M \rightarrow O_3 + M$	·	··
5.	$O_2^* + O_3 \rightarrow 2O_2 + O$	···	····
6.	$O_2^* + M \rightarrow O_2 + M$	—	···

LEGEND: A -- k_0, 1/(mole)(sec); E, kcal

Here M can represent either a molecule of O_3 or O_2, or a molecule of any inert gas. If excited O_2 molecules are formed in reactions 1 and 3, then a chain reaction is possible, which consists of reactions 3 and 5. In this case processes of deactivation can also play a part (reaction 6).
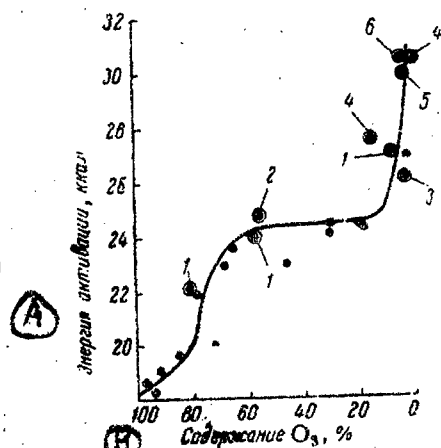
Рис. 1. Зависимость энергии активации от состава смеси:

1—данные Шумахера и Глиссмана[7]; 2—данные Бенсона и Эксворти[4]; 3—данные Клемента[8]; 4—данные Гриффита[9]; 5—данные Вульфа и Толмана[10]; 6—данные Гарвина[11]. (Остальные точки кривой наши данные[6]).
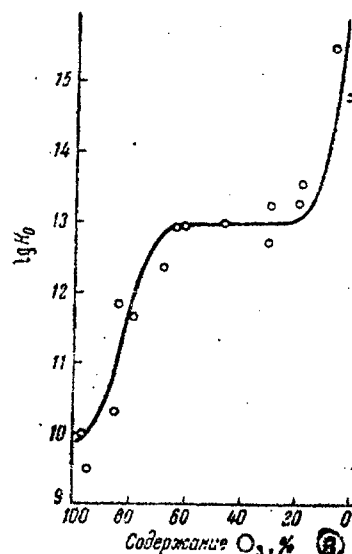
Рис. 2. Зависимость предэкспоненциального множителя константы реакции второго порядка от содержания озона в смеси.

LEGEND: A -- Energy of Activation, kcal; B -- O_3 content, %; C -- Fig. 1. Energy of Activation as Function of Mixture Composition; D -- 1 - Data of Schumacher and

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LEGEND (continued): Glissman(7); 2 — Data of Benson and Axworthy(4); 3 — data of Clement(8); 4 — Data of Griffith(9); 5 — Data of Wulf and Tolman(10); 6 — Data of Garvin(11). (Remaining points on the curve are our data(6)); E —— Fig. 2. Pre-exponential multiplier of the second-order reaction constant as a function of ozone content in the mixture.

The bimolecular reaction 1 obviously has a smaller energy of activation than reaction 2 for which the energy of activation must be not less than the dissociation energy of a O_3 molecule, that is, about 24 kcal/mole. The value of the energy of activation of 18-20 kcal, varying in the decomposition of concentrated ozone, evidently is conditioned on the predominance at the start of the reaction of elementary reaction 1. The pre-exponential multiplier $10^9 - 10^{10}$ is 1 — 2 orders of magnitude less than the number of binary collisions. This fact corresponds to the usual value for the steric factor in such a reaction (of the order of 0.1 — 0.01). Parallelly with the ozone decomposition reaction 1, in pure or very slightly diluted ozone reaction 2 can also occur. In this case M represents an ozone molecule. At comparatively low temperatures reaction 2 evidently is less effective than reaction 1, since reaction 2 requires a greater energy of activation. The decomposition of ozone in reaction 2 proceeds through collisions with oxygen, therefore the role of reaction 2 becomes more important as a measure of oxygen formation. This must lead to an increase in the effective activation energy, which has also been observed in experimentation. When the oxygen content is 15 — 20 %, reaction 2 arising from collisions of ozone molecules with oxygen molecules evidently becomes predominant.

The scheme presented above for the process corresponds to the following equation for the reaction rate:

$$V = -\frac{d[O_3]}{dt} = 2k_1[O_3]^2 + \frac{2k_2\left[1 + \frac{k_6}{k_5}\right][M][O_3]}{\frac{k_6}{k_5} + \frac{k_4}{k_3}\left[1 + \frac{k_4}{k_3}\right]\frac{[O_3][M]}{[O_3]}} . \qquad (4)$$

Here k_i = constants of the corresponding elementary stages.

When $\underline{/O_2\underline{/}} = 0$ and under the condition that excitation processes do not play a part, equation (4) is reduced to a second-order equation

$$V \approx 2(k_1 + k_2)[O_3]^2 \qquad (5)$$

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At relatively low temperatures when reaction 2 based on collisions with ozone is not observed, then the second-order equation is satisfied but with another effective constant:

$$V \approx 2k_1[O_3]^2 \tag{6}$$

From equation (6) we can evaluate approximately k_1 from data at low temperatures which is related to the initial reaction stage.

When $\underline{/O_2\underline{/}} \gg \underline{/O_3\underline{/}}$, where we can assume $\underline{/O_2\underline{/}} \approx$ $\approx$ const, equation (4) also is converted into a second-order equation but with a much more complicated effective "constant" of the second-order reaction:

$$V \approx \left[2k_1 + \frac{2k_2 \cdot k_3}{k_4 \cdot [O_2]} \right] [O_3]^2 = k'[O_3]^2 \tag{7}$$

From the data for the intial period of the reaction according to equation (6) at temperatures up to 100° C we can obtain a value of the pre-exponential multiplier, for k_1, of 4.5×10^9 1/(mole)(sec) and an energy of activation of 18 - 19 kcal. The ratio $\dfrac{k_2}{k_4}$ is the equilibrium constant for the dissociation reaction $O_3 \rightleftharpoons O_2 + O$. Using the values of k' obtained for ozone decomposition in diluted mixtures containing 2 - 3 % O_3, and adopting for k_2 the values obtained for the initial stage of the reaction, and also for k_2/k_4 data from the thermodynamic equilibrium(4), it is possible to calculate the values for k_3 at various temperatures. The calculation has yielded for reaction 3 an energy of activation of 5 $\pm$ 1 kcal.

Attention is now turned on the closeness of the values for the pre-exponential multipliers in reactions 1 and 3 while the energies of activation are widely separated. This indicates that the steric factors for both reactions are close in value.

We will look at the possible explanation for the fact that the value of the pre-exponential multiplier for the second-order constant surpasses the number of binary collisions. Under conditions in which equation (7) is satisfied, that is, in dilute mixtures and at relatively high temperature

$$k_1 < \frac{k_2 \cdot k_3}{k_4 \cdot [O_2]}$$

Consequently

$$k' \approx \frac{2k_2 \cdot k_3}{k_4 \cdot [O_2]}$$

Inserting values for k_3 and k_2/k_4, and for $[O_2]$, we obtain:

$$k' = \frac{2 \cdot 7.7 \cdot 10^4 \cdot e^{\frac{-24\,600}{RT}} \cdot 2.3 \cdot 10^9 \cdot e^{\frac{-5\,000}{RT}}}{3 \cdot 10^{-2}} = 1.85 \cdot 10^{16} \cdot e^{\frac{-29\,600}{RT}} .$$

that is, a high value for the effective energy of activation and a value for the pre-exponential multiplier of the "second-order constant" k_1' that is greater than the number of binary collisions by $10^4 - 10^5$ times. This is a result of the fact that in dilute mixtures a bimolecular reaction actually does not take place. Consequently, the "second-order constant" does not characterize any process occurring through binary collisions but is a combination of constants for various elementary stages. This also explains the change in the value of the effective energy of activation (up to 27 - 31 kcal) as the composition of the mixture changes.

Thus, in order to explain the fact that the pre-exponential multiplier of the second-order constant exceeds the number of binary collisions it is not necessary to introduce an assumption about the existence of chain reactions or the involvement of internal degrees of freedom in the reaction, as this has been done in the studies of Schumacher and Sprenger(12).

If assumptions of chain reactions are not introduced, then stages 5 and 6 are excluded and equation (4) drops out; at this point the expression set forth above for limiting cases is maintained. In the interval of ozone concentrations from 15 to 70 % the reaction rate can be expressed as a second-order equation:

$$V = 1.5 \cdot 10^{13} \cdot e^{\frac{-24500}{RT}} [O_3]^2 \tag{8}$$

Equation (8) has also been used by us in the analysis of data obtained in the enflaming, combustion, and detonation of ozone.

Enflaming of Ozone

The enflaming of gaseous ozone and of its mixtures with oxygen at various pressures and temperatures has been investigated. We enflamed the mixture in a heated vessel with an electric spark. The measurements were carried out in spherical glass vessels that were 34.5, 25.5, and 14.9

mm in diameter(13). Figure 3 shows a graph of the lower limit of enflaming of gaseous ozone in a heated vessel as a function of the temperature of the vessel walls.

In figure 4 the graph of the critical pressure of enflaming as a function of temperature for ozone-oxygen mixtures containing 5 and 10 % ozone is displayed. The dependence of the lower limit of enflaming on the vessel diameter can be expressed by the following relationship:

$$p \cdot d = const \tag{9}$$

As is known, this relationship is satisfied in the enflaming of other burning mixtures also.

In order to clarify the nature of ozone enflaming, the effect of various inert substances and of surface on the position of the lower limit of enflaming has been studied. We used substances which are inert in relation to the ozone decomposition reaction, and which have different heat conductivities, gas-kinetic radii, and heat capacities (O_2, H_2O, CO_2, SO_3, and SiF_4).

As the measurements have indicated, the pressure at the lower limit of enflaming is slightly increased upon introducing large amounts of O_2, CO_2, SO_3, and SiF_4; the effect of water vapor has not been detected. Introducing packing into the reaction vessel does not have a significant effect on the lower limit of enflaming. The measurements indicated that the upper limit to ozone enflaming does not exist. The absence of an upper limit of enflaming and also the absence of any significant effect of the packing, inert gases, and treatment of the vessel walls on the position of the lower limit show that ozone enflaming has the characteristics of a thermal explosion.

The data obtained has been calculated according to the approximate equation of the theory of thermal enflaming due to Semenov(14):

$$\frac{Q \cdot v \cdot k \cdot p^n \cdot E \cdot e \cdot 10^{18}}{N \cdot R \cdot T^{2+n} \cdot x \cdot s} e^{-\frac{E}{RT}} = 1 \tag{10}$$

where p = pressure at the lower limit, mm of Hg.;
       T = temperature, $^{\circ}$K;
       Q = heat effect of the reaction (34.5 cal/mole);
       E = energy of activation, kcal/mole;
       n = reaction order;
       R = gas constant;
       N = 6.023 x 10^{23};
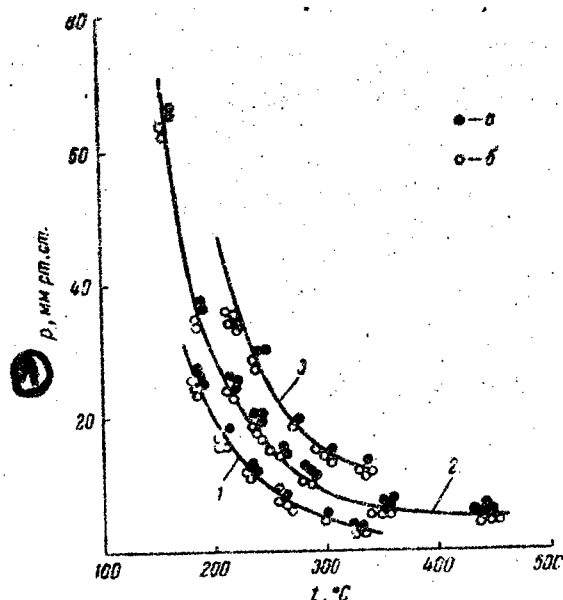   v = vessel volume;
       x = coefficient of heat transfer;

Рис. 3. Зависимость нижнего предела воспламенения озона от температуры при различных диаметрах сосуда:

а—воспламенение; б—отсутствие воспламенения. 1—d= 34,5 мм; 2—d=25,5 мм; 3—d=14,9 мм.

LEGEND: A -- p, mm of Hg.; B -- Fig. 3. Lower limit of ozone enflaming as a function of the temperature using various vassel diameters; C -- a - enflaming; б - absence of enflaming. 1-d = 34.5 mm; 2-d = 25.5 mm; 3-d = = 14.9 mm.

When n = 2, the following relationship must be satisfied

$$\lg \frac{p}{T^2} = \frac{A}{T} + B \tag{11}$$

where

$$A = \frac{E}{n \cdot R} \lg e \cdot \tag{12}$$

$$B = \frac{N \cdot R \cdot x \cdot s}{Q \cdot v \cdot k \cdot e \cdot E \cdot 10^{19}} \tag{13}$$

In figure 5 the dependence of $\lg \frac{p}{T^2}$ on $\frac{1}{T}$ is displayed for an enflaming reaction for undiluted ozone. As is seen from the figure, experimental data corresponds to a linear dependence according to equation (11). Analogous functions have been obtained also for ozone-oxygen mixtures. The slope of the lines have yielded a basis for calculation of the value of A. Adopting n = 2 according to equation (5), we obtain an energy of activation equal to 21 kcal, which is close to the value found for a slow decomposition reaction (24 kcal).
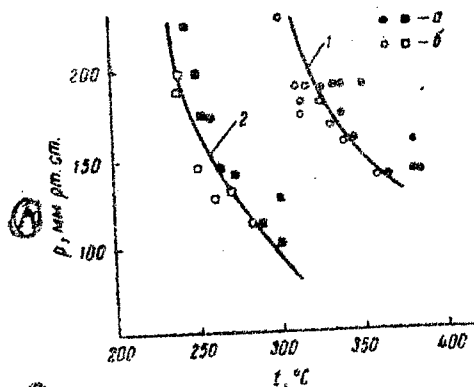
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Рис. 4. Зависимость нижнего предела воспламенения от температуры для озоно-кислородных смесей:

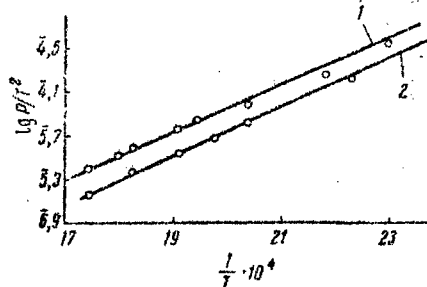а—воспламенение; б—отсутствие воспламенения. 1—5% озона в смеси; 2—10% озона в смеси.

Рис. 5. Зависимость lg $\frac{P}{T^2}$ от $\frac{1}{T}$ для воспламенения озона:

р—критическое давление воспламенения в мм. рт. ст; Т—температура, °К. 1—диаметр сосуда 25,5 мм; 2—диаметр 34,5 мм.

LEGEND: A -- p, mm of Hg; B -- Fig. 4. Lower limit of enflaming as a function of the temperature for ozone-oxygen mixtures; C -- a - enflaming; б - absence of enflaming. 1 - 5 % ozone in mixture; 2 - 10 % ozone in mixture; D -- Fig. 5. Dependence of lg(P/T²) on 1/T for ozone enflaming; E -- p - critical pressure at enflaming, in mm of Hg; T - temperature, °K; 1 - vessel diameter = 25.5 mm; 2 - diameter = 34.5 mm.

As has been shown by Frank-Kamenetskiy(15), thermal explosion in a spherical vessel occurs with a value for the explosion criterion

$$\delta_{\text{кр.}} = \frac{r^2 \cdot k_0 \cdot a^n \cdot Q \cdot E \cdot e^{-\frac{E}{RT}}}{N \cdot R \cdot T^2 \cdot \lambda} = 3{,}32 \qquad (14)$$

where r = vessel radius, cm;
       a = number of molecules per unit volume;
       λ = coefficient of thermal conductivity, cal/(cm)-
                                                   -(sec)(deg).

In table 1 results of the calculation of $\delta_{\text{кр}}$ are presented on the basis of formula (14). The kinetics equation (8) was used in the calculation.

The mean value of $\delta_{\text{кр}}$ = 4.9 satisfactorily agrees with the critical value equal to 3.32.

On the basis of equation (14) the enflaming temperature was calculated for various pressures. The results of the calculations are compared in table 2 with the experimental data.

TABLE 1

Результаты расчета δкр. (A)

Температура °K (B)	Давление на нижнем пределе P мм рт. ст. (C)	Коэффициент теплопроводности $\lambda \cdot 10^6$ кал/см·сек·град. (D)	Теплопроводность, $C_в$ кал/град (E)	Радиус сосуда, r см (F)	δкр.
573	4,8	7,60	9,71	1,75	7,1
523	9,7	7,05	9,41	1,75	6,0
523	15,8	7,05	9,41	1,27	8,3
490	15,5	6,69	9,18	1,75	4,2
49)	23,2	6,69	9,18	1,27	4,9
448	32,6	6,05	8,83	1,75	2,7
435	66,0	5,94	8,73	1,27	3,0

LEGEND: A -- Results of the calculation of δ_{kp};
B -- Temperature, °K; C -- Pressure at lower limit, P in mm of Hg; D -- Coefficient of thermal conductivity, $\lambda \times 10^5$, cal/(cm)(sec)(deg); E -- Thermal conductivity, C_v, cal/deg; F -- Vessel radius, r, cm.
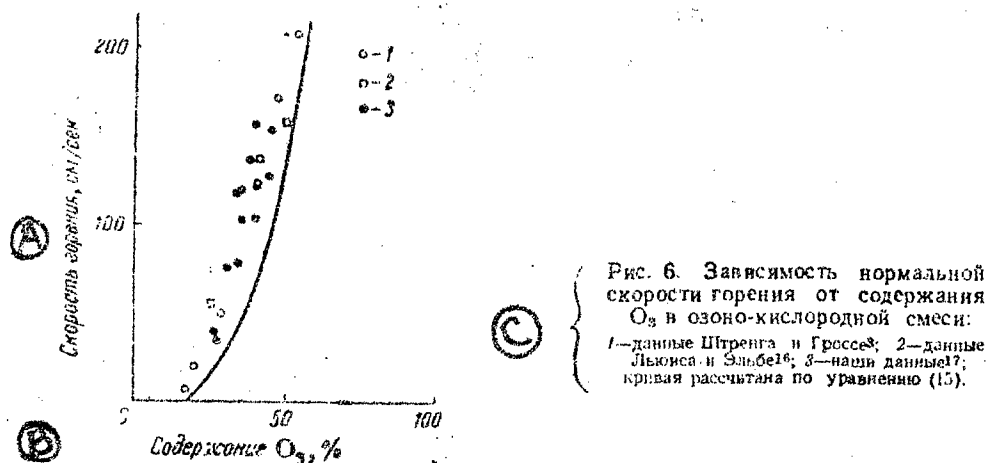
TABLE 2

Зависимость температуры воспламенения от давления (A)

Давление O₃ мм рт. ст. (B)	Температура °K (E)		Давление O₃ мм рт. ст. (F)	Температура °K (E)	
(E)	опытная (C)	вычисленная (D)	(F)	опытная (C)	вычисленная (D)
Диаметр сосуда 34,5 мм (F)			Диаметр сосуда 25,5 мм		
32,0	448	453	66	435	438
15,5	490	484	37,6	459	458
12,0	505	498	23,2	490	479
9,7	523	509	19,2	515	489
7,0	548	525	15,8	523	500
4,8	573	547	12,0	548	515
			10,0	553	524
			8,5	573	533

LEGEND: A -- Enflaming temperature as a function of pressure; B -- O₃ pressure, mm of Hg; C -- Experimental; D -- Calculated; E -- Temperature, °K; F -- Vessel diameter = 34.5 mm, vessel diameter = 25.5 mm.

As is seen from table 2, we have a satisfactory agreement between the experimental and the calculated values. This shows that the critical condition of ozone enflaming and also for its mixtures with oxygen is found in satisfactory agreement with the data relating to the kinetics of the slow reaction of ozone decomposition.

Rate of Ozone Combustion

In order to clarify what kind of relationship there exists between the kinetics of the slow reaction and the rate of ozone combustion data is needed on the rate of flame propagation in ozone and in ozone-oxygen mixtures. Since the literature reveals only the limited data of L'yuis and El'be(16), we conducted measurements of the rate of ozone combustion in mixtures containing oxygen. The rate of flame propagation was measured in a horizontal tube with an open end. In view of the small flame activity a photoelectric method(17) was used (fig. 6).

Рис. 6. Зависимость нормальной скорости горения от содержания O₃ в озоно-кислородной смеси: 1—данные Штренга и Гроссе³; 2—данные Льюиса и Эльбе¹⁶; 3—наши данные¹⁷; кривая рассчитана по уравнению (15).

After we carried out this study there was published data of Streng and Grosse(3), which they obtained by a burner method /metodom gorelki_7. On the basis of the graph we can arrive at the conclusion that the values of the normal combustion rate that were obtained by various methods agree among each other.

The assumption of the invariance of the reaction kinetics under combustion conditions made feasible the theoretical calculation of the combustion rate based on kinetic data. Such a calculation has been done by Karman (18); the data agrees satisfactorily with the data of the

study(3).

We carried out calculations of the normal combustion rate on the basis of the equations of Zel'dovich—Frank—Kamenetskiy(19).

A condition of the applicability of the approximation equations of this theory is the criterion expressed by the equation

$$\frac{R \cdot T}{E} \leqslant 0,1$$

where T = combustion temperature;
and E = energy of activation, kcal.

Adopting the value of 24.5 kcal for the energy of activation, we obtain for this criterion for mixtures containing from 18 to 100 % ozone, values from 0.085 to 0.223. For concentrations which we used for the measurements (from 26 to 45 % O_3) the mean value of the criterion was approximately 0.1. Thus, the use of the approximation equations is permissible.

The calculation of the combustion rate was carried out on the basis of the equation:

$$U_n = \sqrt{\frac{2\lambda^* C_p^{*2}(k \cdot a_0)}{\rho_0 \cdot L^3} e^{-\frac{E}{RT_r}} \left(\frac{RT_r^2}{E}\right)^3 \left(\frac{T_0}{T_r}\right)^2 \left(\frac{A}{B}\right)^2 \left(\frac{n_1}{n_2}\right)^2} \qquad (15)$$

where U_n = normal combustion rate, cm/sec;

λ^* = coefficient of thermal conductivity of the combustion products, kcal/(cm)(sec)(deg);

C_p^* = heat capacity of combustion products, kcal/(g)-(deg);

k = pre-exponential multiplier in the Arrhenius equation, cm^3/(mole)(sec);

a_0 = initial ozone concentration, mole/cm^3;

E = 24.5 kcal/mole;

ρ_0 = density of the mixture of starting materials, g/cm^3;

L = heat effect of the reaction, kcal/g;

T_0 = initial combustion temperature, $^\circ$K;

n_1 and
n_2 = number of moles, respectively, of the starting materials and the reaction products

$$\frac{A}{B} = \frac{\lambda}{C_p \rho D}$$

where D = coefficient of ozone diffusion in oxygen.

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In the calculation the equation of the reaction rate (8) was assumed; and the combustion temperatures were calculated in an adiabatic approximation, taking into account the dissociation of oxygen. The calculation results based on equation (15) are shown in fig. 6.

The calculated dependence of U_n on the mixture composition agrees approximately with the experimental. However, the absolute values are less than the experimental values. A comparison of the data with the calculated values of Karman[18] have indicated that in adopting the approximation the calculated values have deviated from the experimental on the opposite side. At the same time the values of the deviations from the experimental values is less than those in the approximation that corresponds to equation (15).

In comparing the studies obtained in the studies (3,17) we can arrive at the conclusion that the ozone combustion rate in mixtures with oxygen corresponds to the kinetics of the reaction of the thermal decomposition of ozone.

Detonation of Liquid Ozone

According to Khariton[20] the critical condition of detonation of explosive substances is also dependent on the kinetics of the chemical reaction leading to the explosion. If the kinetics of ozone decomposition under these conditions is the same, then there must exist a relationship between the kinetics conditions, namely, the critical diameter of the charge in which a stable ozone detonation can occur, and the data set forth above that concerns the thermal decomposition kinetics for ozone. This dependence can be expressed by the following equation:

$$d_\kappa = \frac{A \cdot R \cdot T_E^2}{T_e \cdot E} e^{\frac{E}{RT_E}} \tag{16}$$

where d_k = critical charge diameter, mm;

    A = constant;

    T_E = temperature at front of detonation wave, $^\circ K$;

    T_e^E = temperature close to the temperature of the explosion products, $^\circ K$;

    E = energy of activation for the chemical reaction, kcal;

and R = gas constant.

Inasmuch as not all constants that enter into equation (16) are known, investigation of this problem can be

conveniently conducted by using a mixture of ozone with inert substances of various concentrations.
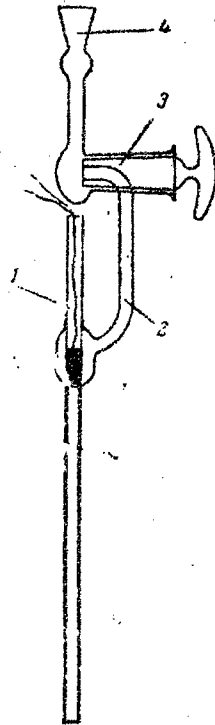

Рис. 7. Прибор для исследования взрывов озона:

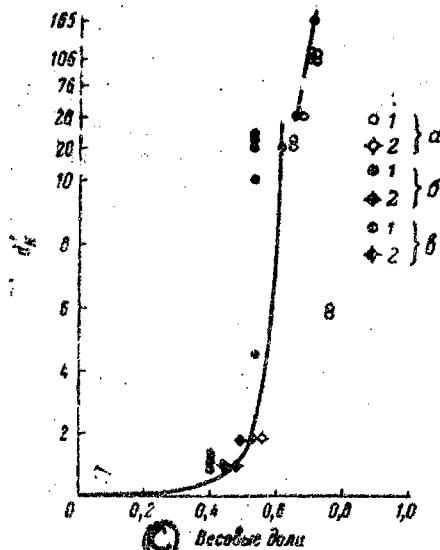*1*—трубка для инициатора; *2*— трубка для ввода озона и других веществ; *3*—вакуумный кран; *4*—шлиф.

Рис. 8. Зависимость критического диаметра заряда от содержания различных разбавителей:

а—отсутствие устойчивой детонации; *б*—прохождение детонации; *в*—затухающая детонация: *1*—кислород; *2*—четырехфтористый углерод.

LEGEND: A -- Fig. 7. Device for study of ozone explosions; B -- 1 - tube for initiator; 2 - tube for the inlet of ozone and other substances; 3 - vacuum screen; 4 - ground end; C -- Weight fractions; D -- Fig. 8. Critical charge diameter as a function of the content of various diluents; E -- a - absence of stable detonation; *б*- occurrence of detonation; *в*- attenuating detonation: 1 - oxygen; 2 - carbon tetrachloride.

Letting α stand for the weight fraction of the explosive substance in the mixture, and assuming for the mixture that

$$T'_E = \alpha \cdot T_E \quad \text{and} \quad T'_e = \alpha \cdot T_e$$

Khariton obtained the following equation for the critical charge diameter in which the mixture of the explosive substance with an inert substance is detonated:

$$d'_\kappa = d_\kappa \cdot \alpha \cdot e^{\frac{E}{RT_E}\left(\frac{1-\alpha}{\alpha}\right)} \tag{17}$$

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here d_K = critical diameter for pure explosive substance.

The methods of determining the critical diameter consists of establishing the presence of a continuous trace of the detonation on a brass plate secured to a glass cylindrical ampule containing liquid ozone or its mixtures. We used glass tubes of various diameters. The length of the filled portion was at a level from 10 to 30 cm. The filled tube containing the liquid was placed in a steel container filled with liquid oxygen. Initiation of the reaction was effected by explosion of lead azide or a detonator capsule. In several experiments we used a supplementary detonator -- a hexogen cartridge. Figure 7 shows one of the devices in which the explosion took place.

The experiments carried out indicated that the detonation of liquid ozone proceeds in charges having a diameter of approximately 0.15 mm. Evidently, the critical diameter for liquid ozone is somewhat less than this value.

The results of the experiments with various diluents of liquid ozone are exhibited in fig. 8. The curve was drawn on the basis of equation (17). The following values were used for the calculation: E = 24000 cal/mole, T = 3000 $^\circ K$ (theoretical temperature for ozone combustion), and d_K = 0.15 mm for pure ozone; α = weight fraction of ozone in the solution. The calculation naturally is approximate.

It is easy to see that the calculated curve fairly sharply divides the region of ozone concentrations in which the detonation occurs from the region of ozone concentration in which detonation does not occur. From the data obtained it follows that the value of the critical diameter of the mixture, d_K, is basically determined by the weight fraction of the explosive substance and by the kinetics of its decomposition, as follows from equation (17).

Thus, the dependence between the detonation properties of liquid ozone and the kinetics of its thermal decomposition is found to be in accord with the theory of critical diameters.

Conclusions

1. Data presented in the article indicates that kinetic principles of the ozone decomposition reaction determine the principles of ozone enflaming, combustion, and detonation. This is conditioned in the first place in the fact that the reaction mechanism evidently varies little under these conditions.

2. The theories which were used here for the analysis of experimental data and for the comparison of the data with the kinetics of the ozone decomposition reaction lead, in general, validly both to general principles and to quantitative functions.

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